

Correspondence: Reply to 'Strongly-driven Re + CO₂ redox reaction at high-pressure and high-temperature'

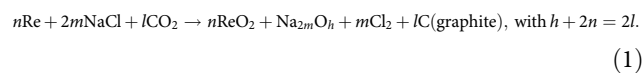
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Santamaria-Perez *et al.*¹ attempt to reproduce our CO₂-SiO₂ solid solution². In their study¹, mixtures of CO₂ and SiO₂ similar to those studied in our work² were indirectly laser heated up to 2,400 K and 50 GPa by using Re as an internal heater, and a CO₂-SiO₂ solid solution was not obtained. Instead, the only temperature quenched crystalline phases identified by X-ray diffraction were: known polymorphs of pure CO₂ and SiO₂, Re and ReO₂. In particular, the structure of ReO₂ was identified as being the β -ReO₂ (Pbcn), which is a well known phase of this oxide discovered many decades ago (ref. 9 in the letter). ReO₂ was then inferred to form from a high P-T, Re + CO₂ redox reaction. Moreover, it is shown that β -ReO₂ may provide a better fit to our XRD pattern than the cristobalite-like CO₂-SiO₂ solid solution. A shadow is then cast on the very existence of this solid solution.

In light of this study¹, we have reanalysed all our data, and realized that more complex chemical reactions may have occurred in our samples due to the extreme high temperatures: T > 4,000 K. To make the reaction between CO₂ and SiO₂ as efficient as possible, we understood that starting from confined CO₂ in a SiO₂ zeolite was not sufficient and then we planned and managed to heat the sample at conditions where both CO₂ and SiO₂ are fluid. The aim was to react them together starting from an ideal, hot, highly mobile mixture. For achieving very high temperatures, we insulated diamond using thick NaCl layers pelleted on it. Then, in principle, we carefully avoided laser heating the Re gasket. Nevertheless, we recognize that the laser spot may have hit the gasket at some point and/or the hot fluid sample may have drifted toward the gasket where spurious reactions with Re may have occurred. We have now reanalysed all our XRD patterns, including those at room pressure where potential volatile components (for example, CO₂) are absent making data interpretation as simple and clean as possible. Indeed, we confirm

that the β -ReO₂ provides a better fit to the new phase than cristobalite. The lack of XRD Bragg peaks of stishovite in our samples, which was found in the letter by Santamaria-Perez, may be easily explained with liquid SiO₂ being temperature quenched in a glassy form. Our results thus do not prove the existence of a CO₂-SiO₂ solid solution and β -ReO₂ is indeed one of the materials synthesized in our experiment. Also, Raman data show that the chemistry was even more complex in our study. We now have an alternative explanation for the dominant Raman peak with five, fine-structure components². This spectrum matches exactly that of crystalline Cl₂ (ref. 3), which clearly came from a partial dissociation of the NaCl insulating layers. Incidentally, we note that very recent studies show that simple salts, such as NaCl and KCl, may undergo major chemical changes upon laser heating at high pressures^{4,5} (see also ref. 5 for an updated Raman spectrum of solid Cl₂). We recall, as noted in our original paper², that some microcrystalline/amorphous carbon was also formed in our laser-heated sample. In conclusion, we think that our revised data interpretation is consistent with the very complex chemistry that occurred in our study under extreme conditions, one potential chemical reaction path being CO₂ decomposed and, as a result, both Re from the gasket and NaCl were partially oxidized by the available free oxygen. Pure, molecular chlorine was then released after oxidation of NaCl. Decomposition of CO₂ and oxidation of Re and NaCl finally led to free carbon available to form graphite. We can resume this potential reaction as:



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Additional information

Competing financial interests: The authors declare no competing financial interests.

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